

## Structure of Dilithium Tetraammonium *cyclo*-Hexaphosphate Tetrahydrate

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(Received 12 November 1991; accepted 22 July 1992)

**Abstract.**  $\text{Li}_2(\text{NH}_4)_4\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$ ,  $M_r = 631.93$ , monoclinic,  $P2_1/c$ ,  $a = 9.429$  (2),  $b = 15.824$  (3),  $c = 7.931$  (1) Å,  $\beta = 106.26$  (1)°,  $V = 1136$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.85$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 0.562$  mm<sup>-1</sup>,  $F(000) = 648$ ,  $T = 294$  K, final  $R = 0.041$  for 2504 independent reflections,  $wR = 0.045$ . The main structural units are a centrosymmetric  $\text{P}_6\text{O}_{18}$  ring anion and different coordination polyhedra,  $\text{LiO}_4$ ,  $\text{N}(1)\text{O}_5$  and  $\text{N}(2)\text{O}_6$ . The  $\text{P}_6\text{O}_{18}$  ring anions are interconnected by two ammonium polyhedra, the  $\text{LiO}_4$  tetrahedra and hydrogen bonds. The hydrogen-bond scheme is described.

**Introduction.** This work is part of a systematic investigation of mixed monovalent *cyclo*-hexaphosphates. Up to now, only six structure types of these compounds with mixed cations are known:  $\text{Li}_3\text{M}'_3\text{P}_6\text{O}_{18}\cdot 12\text{H}_2\text{O}$  ( $M' = \text{Na}, \text{K}$ ) (Averbuch-Pouchot, 1989a),  $\text{Ag}_3(\text{NH}_4)_3\text{P}_6\text{O}_{18}\cdot \text{H}_2\text{O}$  (Averbuch-Pouchot, 1991),  $\text{Li}_2\text{Ag}_4\text{P}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$  (Averbuch-Pouchot & Durif, 1991b) and  $\text{Na}_2\text{Tl}_4\text{P}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$  and  $\text{Rb}_2\text{Na}_4\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$  (Averbuch-Pouchot & Durif, 1991a). This work is devoted to a detailed structural investigation of dilithium tetraammonium *cyclo*-hexaphosphate tetrahydrate. The preparation, main crystallographic features and physical-chemical properties of the title compound will be described elsewhere (Elmokhtar & Rzaigui, 1992).

**Experimental.** Crystal size  $0.18 \times 0.24 \times 0.26$  mm.  $D_m$  not measured. Philips PW1100 diffractometer, graphite-monochromatized Mo  $K\alpha$  radiation, 25 reflections with  $\theta$  in the range  $10 < \theta < 12^\circ$  used for determining lattice constants and orientation matrix, 3029 unique reflections measured ( $3 < \theta < 30^\circ$ ),  $\pm h, k, l$ ,  $h_{\text{max}} = 18$ ,  $k_{\text{max}} = 30$ ,  $l_{\text{max}} = 18$ ,  $\omega$  scan, scan width  $1.2^\circ$ , scan speed  $0.02^\circ \text{ s}^{-1}$ , total background measuring time 6 s, intensities of two reference

reflections (252,  $\bar{2}52$ ) measured every 4 h showed no significant variation. Lorentz and polarization corrections, no absorption correction. Structure solved by classical methods (Patterson and successive Fourier syntheses). H atoms from difference Fourier map. Anisotropic full-matrix least-squares refinement (on  $F$ ), isotropic for H atoms. Unit weight. Final refinement cycles with 2504 reflections corresponding to  $F > 3\sigma_F$ . Final  $R = 0.041$ ,  $wR = 0.045$ ,  $S = 1.227$ . Max.  $\Delta/\sigma = 0.13$ , max. peak height in the final difference Fourier synthesis  $0.35 \text{ e } \text{Å}^{-3}$ . Extinction correction  $g = 10^{-6}$ . Scattering factors for neutral atoms and  $f'$ ,  $f''$  from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf-Nonius (1980) SDP employed for all calculations. MicroVAX 2000 computer used.

**Discussion.** Final atomic coordinates are given in Table 1.† Fig. 1 represents the projection of the atomic arrangement along the  $a$  axis. Lithium and ammonium polyhedra are depicted in Fig. 2. Main interatomic distances, bond angles in the  $\text{P}_6\text{O}_{18}^{6-}$  anion and hydrogen bonds are reported in Table 2.

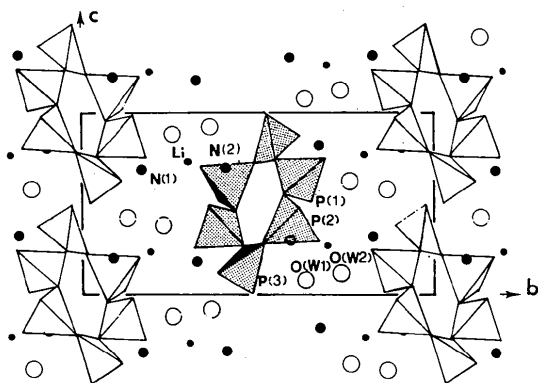
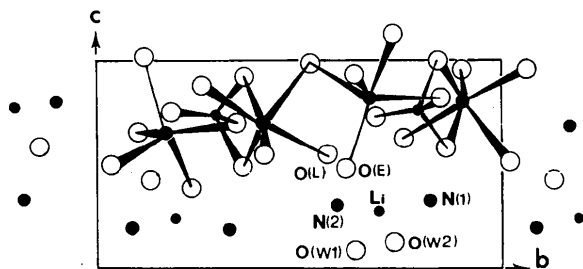
The local geometry around the  $\text{PO}_4$  tetrahedra ( $\text{P—O}$  and  $\text{O—O}$  distances,  $\text{O—P—O}$  and  $\text{P—O—P}$  angles) is similar to that commonly observed in cyclic or linear condensed phosphoric anions. The bridging  $\text{P—O}$  bonds in the tetrahedra are longer than the terminal bonds and the largest  $\text{O—P—O}$  angles in the tetrahedra correspond to the shortest  $\text{P—O}$  and the longest  $\text{O—O}$  distances (Table 2). This is probably explained by the effect of mutual repulsion of the non-bridging O atoms. The phosphoric ring is made up of six corner-sharing  $\text{PO}_4$  tetrahedra. The  $\text{P}_6\text{O}_{18}^{6-}$  ring anion is centrosymmetrical, so it is

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55625 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU0331]

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Table 1. Final atomic coordinates and  $B_{eq}$  values for  $\text{Li}_2(\text{NH}_4)_4\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$  with *e.s.d.*'s in parentheses
$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}$ ( $\text{\AA}^2$ )
P(1)	0.5046 (1)	0.3808 (8)	0.6299 (9)	1.10 (1)
P(2)	0.2109 (8)	0.4008 (3)	0.3975 (5)	1.35 (1)
P(3)	0.7615 (3)	0.4665 (2)	0.8524 (4)	1.29 (1)
O(E11)	0.5734 (5)	0.3543 (9)	0.4910 (8)	1.62 (4)
O(E12)	0.4770 (8)	0.3147 (3)	0.7491 (3)	2.03 (4)
O(L12)	0.3555 (6)	0.4324 (3)	0.5461 (9)	1.65 (4)
O(L23)	0.1695 (7)	0.4850 (2)	0.2842 (4)	1.61 (4)
O(E21)	0.2531 (1)	0.3315 (8)	0.8960 (9)	1.99 (4)
O(E22)	0.0911 (4)	0.3872 (4)	0.4812 (9)	2.38 (4)
O(E31)	0.2380 (4)	0.4778 (9)	0.9973 (2)	1.91 (4)
O(E32)	0.8321 (1)	0.3829 (4)	0.8811 (5)	2.06 (4)
O(L13)	0.5913 (5)	0.4581 (2)	0.7419 (6)	1.47 (4)
O(W1)	0.4838 (4)	0.1319 (6)	0.5812 (7)	2.56 (5)
O(W2)	0.8185 (2)	0.2623 (4)	0.1204 (3)	3.01 (5)
N(1)	0.0992 (1)	0.3278 (2)	0.8178 (7)	2.38 (6)
N(2)	0.7906 (2)	0.0886 (1)	0.8099 (5)	2.37 (5)
Li	0.4481 (3)	0.3029 (7)	0.2692 (6)	1.8 (1)

Fig. 1. Projection along the  $a$  axis of the atomic arrangement of  $\text{Li}_2(\text{NH}_4)_4\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$ .Fig. 2. Projection along the  $a$  axis of the associated cations.

located by only three crystallographically independent  $\text{PO}_4$  tetrahedra,  $\text{P}(1)\text{O}_4$ ,  $\text{P}(2)\text{O}_4$  and  $\text{P}(3)\text{O}_4$ . The  $\bar{1}$  internal symmetry is the most frequently observed symmetry;  $m$ ,  $m/3$ , 3, 3 and twofold local symmetry have also been seen in the  $\text{P}_6\text{O}_{18}^{6-}$  anions characterized already. The values of the three P—P—P angles are different and are quite similar to those measured in a  $\text{P}_6\text{O}_{18}^{6-}$  anion with the same internal symmetry. However, they are significantly different from what is observed in a  $\text{P}_6\text{O}_{18}^{6-}$  anion with different internal symmetry where, for instance, the

Table 2. Main interatomic distances ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) in  $\text{Li}_2(\text{NH}_4)_4\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$ 

$\text{P}(1)\text{O}_4$ tetrahedron				
P(1)	O(E11)	O(L12)	O(L13)	
O(E11)	1.487 (3)	117.7 (1)	111.5 (1)	
O(E12)	2.539 (4)	1.480 (2)	109.6 (1)	109.8 (1)
O(L12)	2.539 (4)	2.517 (3)	1.600 (2)	95.5 (1)
O(L13)	2.546 (3)	2.516 (3)	2.364 (3)	1.593 (2)
$\text{P}(2)\text{O}_4$ tetrahedron				
P(2)	O(E11)	O(E22)	O(L12)	O(L23)
O(E21)	1.478 (3)	119.6 (2)	109.0 (1)	111.9 (1)
O(E22)	2.554 (4)	1.477 (3)	108.2 (1)	106.1 (1)
O(L12)	2.517 (4)	2.502 (3)	1.611 (2)	100.2 (1)
O(L23)	2.546 (3)	2.453 (4)	2.458 (3)	1.592 (2)
$\text{P}(3)\text{O}_4$ tetrahedron				
P(3)	O(E31)	O(E32)	O(L23)	O(L13)
O(E31)	1.481 (2)	120.7 (1)	110.4 (1)	105.5 (1)
O(E32)	2.564 (3)	1.469 (2)	106.5 (1)	110.5 (1)
O(L23)	2.536 (3)	2.466 (3)	1.606 (3)	101.7 (1)
O(L13)	2.457 (3)	2.527 (3)	2.490 (3)	1.605 (2)
Averages				
	P—O	O—O	O—P—O	
$\text{P}(1)\text{O}_4$	1.540 (3)	2.503 (4)	109.11 (1)	
$\text{P}(2)\text{O}_4$	1.539 (3)	2.505 (4)	109.17 (1)	
$\text{P}(3)\text{O}_4$	1.540 (3)	2.506 (3)	109.20 (1)	
P—P—P				
P(1)—P(2)	2.882 (1)	P(2)—P(3)	2.947 (1)	
P(1)—P(3)	2.902 (1)	Average	2.910 (1)	
P—O—P				
P(2)—P(1)—P(3)	145.76 (3)	P(1)—O(L12)—P(2)	127.7 (1)	
P(1)—P(2)—P(3)	105.00 (3)	P(1)—O(L13)—P(3)	130.4 (1)	
P(1)—P(3)—P(2)	97.97 (3)	P(2)—O(L23)—P(3)	134.3 (2)	
$\text{LiO}_4$ polyhedron				
Li—O(E11)	1.997 (5)	Li—O(E21)	1.961 (6)	
Li—O(E12)	1.896 (6)	Li—O(W1)	1.918 (6)	
$\text{N}(1)\text{O}_5$ polyhedron				
N(1)—O(E21)	2.937 (4)	N(1)—O(E32)	2.838 (4)	
N(1)—O(E22)	2.812 (4)	N(1)—O(W2)	3.020 (4)	
N(1)—O(E31)	2.885 (4)			
$\text{N}(2)\text{O}_6$ polyhedron				
N(2)—O(E11)	2.950 (4)	N(2)—O(E31)	2.953 (4)	
N(2)—O(L12)	3.187 (4)	N(2)—O(W1)	3.029 (3)	
N(2)—O(E22)	2.805 (3)	N(2)—O(W2)	2.856 (4)	
Water				
H(1W1)—O(W1)—H(2W1)	109 (5)			
H(1W2)—O(W2)—H(2W2)	118 (5)			
D—H...A				
N(1)—H(1N1)...O(E22)	0.82 (6)	2.02 (6)	2.812 (4)	162 (5)
N(1)—H(2N1)...O(E21)	0.90 (5)	2.06 (5)	2.938 (4)	168 (5)
N(1)—H(3N1)...O(E31)	0.96 (5)	2.00 (5)	2.885 (4)	153 (5)
N(1)—H(4N1)...O(W2)	0.76 (6)	2.59 (5)	3.020 (4)	118 (5)
N(2)—H(1N2)...O(E22)	0.91 (4)	1.92 (4)	2.805 (3)	164 (4)
N(2)—H(2N2)...O(W2)	0.89 (5)	1.97 (5)	2.856 (4)	175 (4)
N(2)—H(3N2)...O(E31)	0.92 (6)	2.05 (6)	2.953 (4)	168 (5)
N(2)—H(4N2)...O(E11)	0.91 (7)	2.11 (7)	2.950 (4)	154 (5)
O(W1)—H(1W1)...O(E31)	0.75 (5)	2.02 (5)	3.191 (3)	167 (5)
O(W1)—H(1W1)...O(E31)	0.97 (6)	1.85 (6)	2.823 (3)	176 (5)
O(W2)—H(1W2)...O(E32)	0.82 (5)	1.91 (5)	3.067 (4)	169 (5)
O(W2)—H(2W2)...O(E11)	0.76 (6)	2.18 (6)	2.915 (3)	162 (6)

P—P—P angles are  $108.51^\circ$  in  $(\text{NH}_4)_4\text{P}_6\text{O}_{18}\cdot \text{H}_2\text{O}$  (Averbuch-Pouchot, 1989b) and  $87.47$ ,  $114.38$  and  $115.57^\circ$  in  $\text{Ce}_2\text{P}_6\text{O}_{18}\cdot 10\text{H}_2\text{O}$  (Bagieu-Beucher & Rzaigui, 1992).

The Li atom is tetrahedrally coordinated by one water molecule O(*W1*) and three external O atoms O(*E11*), O(*E21*) and O(*E12*) belonging to two  $\text{P}_6\text{O}_{18}^{6-}$  ring anions. The  $\text{LiO}_4$  tetrahedron is as regular as the  $\text{PO}_4$  tetrahedron. Within a sphere coordination of 3.5 Å, the two ammonium cations have different environments, namely N(1) $\text{O}_5$  and N(2) $\text{O}_6$ . The first, N(1), is coordinated to one water molecule O(*W2*) and four external O atoms [O(*E21*), O(*E22*), O(*E31*), O(*E32*)] belonging to three  $\text{P}_6\text{O}_{18}$  rings. O(*E21*) is a vertex common to an  $\text{LiO}_4$  tetrahedron and an N(1) $\text{O}_5$  polyhedron. The second, N(2), has sixfold coordination, formed by two water molecules [O(*W1*), O(*W2*)] and four O atoms [O(*E11*), O(*L12*), O(*E31*), O(*E22*)] from two  $\text{P}_6\text{O}_{18}$  rings. The N(2) $\text{O}_6$  distorted octahedron and  $\text{LiO}_4$  tetrahedron contact one another *via* the common edge O(*E11*)—O(*W1*). The N(1) $\text{O}_5$  and N(2) $\text{O}_6$  polyhedra are interconnected by the  $\text{LiO}_4$  tetrahedra (Fig. 2). The alternating N(1) $\text{O}_5$ ,  $\text{LiO}_4$  and N(2) $\text{O}_6$  form chains running along the *b* axis. The shortest N(2)—Li, Li—N(1) and N(1)—N(2) distances and the largest N(1)—N(2)—Li, N(2)—Li—N(1) and Li—N(1)—N(2) angles are,

respectively, 3.590 (6), 3.994 (6) and 4.438 (4) Å for the bonds and 133.3 (1), 169.4 (2) and 165.3 (1)° for the angles. So the  $\text{P}_6\text{O}_{18}$  ring anions are interconnected by the  $\text{LiO}_4$  tetrahedron, the two ammonium polyhedra and the hydrogen bonds, forming the  $\text{Li}_2(\text{NH}_4)_4\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$  three-dimensional network.

The authors thank Dr A. Durif (CNRS Grenoble, France) for the data collection.

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*Acta Cryst.* (1993). **C49**, 437–439

## Structure of $\text{Nb}_5(\text{Ge}_x\text{Sn}_{1-x})_2\text{Ge}$ , $x = 0.25$

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(Received 16 May 1991; accepted 11 August 1992)

**Abstract.**  $\text{Nb}_5\text{Ge}_{1.5}\text{Sn}_{1.5}$ ,  $M_r = 751.45$ , tetragonal,  $I4/mcm$ ,  $a = 10.451$  (1),  $c = 5.1920$  (7) Å,  $V = 567.0$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 8.80$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 24.05$  mm<sup>-1</sup>,  $F(000) = 1312$ , room temperature, final  $R = 0.044$ ,  $wR = 0.042$  for 245 [ $|F_o| > 3\sigma(F_o)$ ] unique reflections. The title compound is isomorphous with  $\text{W}_5\text{Si}_3$ . The 16(*k*) and 4(*a*) sites are only occupied by Nb, and the 4(*b*) sites only by Ge. The 8(*h*) sites are randomly occupied by atoms of both Ge and Sn with an atomic ratio of 1:3. Atoms with large atomic radii are not accommodated by the 4(*a*) sites in a  $\text{W}_5\text{Si}_3$ -type structure.

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**Introduction.** The intermetallic compounds in the Nb–Sn–Ge ternary system are studied because of the possibility of their being superconductive materials. But as yet, not many compounds in this system have been synthesized. So the synthesis of the compounds in the system was performed and single crystals of a new compound of composition Nb:Sn:Ge = 10:3:3 were obtained. The crystal structure was analyzed by a single-crystal X-ray diffraction method. This paper reports the results of the crystal-structure analysis.

**Experimental.** Crystals of  $\text{Nb}_5(\text{Ge}_x\text{Sn}_{1-x})_2\text{Ge}$ ,  $x = 0.25$ , were synthesized by the self-component flux method (Sn as flux). Nb and Ge were mixed with an atomic ratio of 3:1 and Sn was added to these